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Ultrafiltration

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Introduction

Ultrafiltration (UF) is a filtration process that employs a membrane to fractionate liquid mixtures containing molecules that range in size from about 1000 daltons in molecular weight to 500 000 daltons. The membrane, made of either polymeric or inorganic materials, is a semipermeable barrier containing pores of a certain size distribution that are used to retain or 'reject' components of the feed mixture that are larger than the rated pore size while allowing molecules that are smaller than the pores to pass through the membrane. This separation process is very simple (**Figure 1**) involving only the pumping of fluids. The membrane is assembled in a particular configuration and placed in a module, and the feed stream is pumped through the module over the membrane surface in a cross-flow mode. The pressure forces solvent (e.g. water) and solute molecules smaller than the pores on the membrane surface through the membrane into the 'permeate' stream while larger solutes are rejected and retained in the 'retentate' stream. The retentate is recycled through the module until the required degree of purification, separation or concentration is achieved.

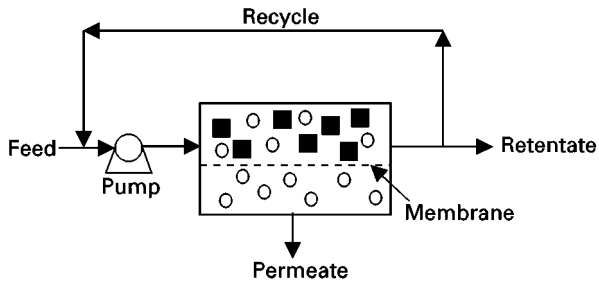

Figure 1 Cross-flow ultrafiltration. Particles in the feed that are larger than the rated pore size of the membrane are retained in the retentate stream while smaller particles pass through into the permeate. (Adapted from Cheryan (1998) with permission from Technomic.)

Ultrafiltration is similar in concept to other pressure-driven membrane processes such as microfiltration, nanofiltration and reverse osmosis. However, as shown in **Figure 2**, the size range of the solutes that are retained by each membrane is different. Reverse osmosis (RO) membranes are designed to retain all components except for the solvent (e.g. water). It is essentially a concentration process. Owing to the osmotic pressure of the solutes retained by RO membranes, pressures needed to operate RO systems are typically 30–60 bar (450–900 lb in^{-2}). Nanofiltration (NF) membranes have slightly larger pores and are designed to allow monovalent salts such as sodium chloride to pass through, but retains divalent salts, disaccharides and dissociated organic acids. Pressures are usually lower, about 15–25 bar. Microfiltration (MF) membranes retain components that are in suspension or in colloidal form, and is essentially a clarification process. Pressures are usually 1–4 bar.

Ultrafiltration, on the other hand, is designed to retain macromolecules and other solutes in the size range of 1–50 nm, or with equivalent molecular weights of 1000 to 500 000 daltons. It also operates at low pressures (2–6 bar) and can simultaneously act as a concentration, purification and fractionation process, depending on the components in the feed and the membrane properties. It has several advantages over other separation or concentration techniques. Unlike freeze concentration or evaporation, there is

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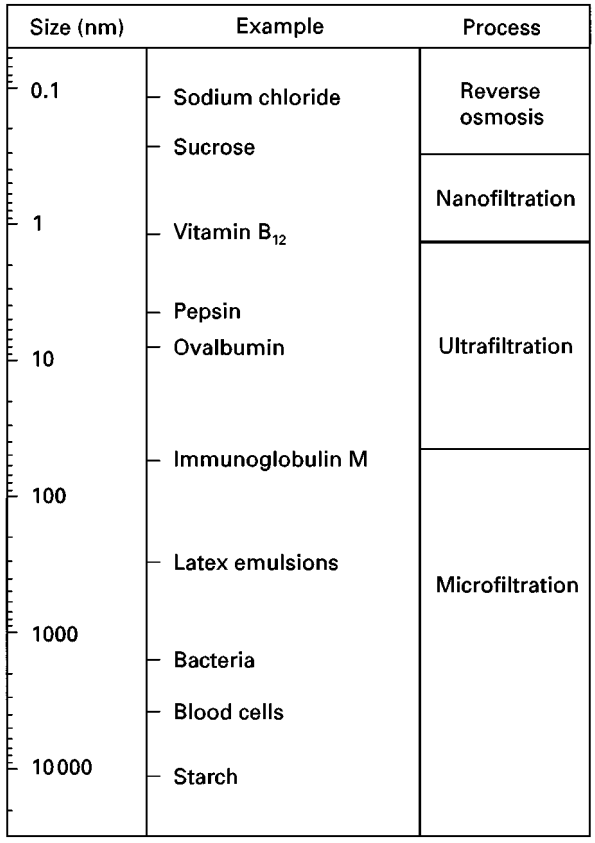

Figure 2 Examples of compounds of various sizes separated by different membranes. (Adapted from Cheryan (1998) with permission from Technomic.)

no change in phase of the solvent and thus energy consumption is much lower. Being a nonthermal process, there are no extremes of temperature and feed solutions can be concentrated by UF with little or no thermal damage to heat-sensitive components. Since pores are large enough to allow passage of soluble salts, acids and alkalis, the microenvironment of the solution remains largely unchanged during the process.

There are several factors that affect ultrafiltration applications: the membrane material, properties of the membrane, process engineering parameters, design of the membrane module, fouling and cleaning and process design. The most important performance parameters in UF are flux and rejection. Flux is the volume of permeate per unit time per unit membrane area. Higher flux means lower capital and operating costs. Rejection is a measure of a membrane's separating capabilities. It is defined as:

$$1 - \frac{\text{Concentration of solute in the permeate}}{\text{Concentration of solute in the retentate}}$$

Membrane Material

Membranes have been made from over 150 different polymers or inorganic materials, but only about a dozen have achieved widespread commercial use for UF. The most common are polymers such as polysulfone, polyethersulfone, polyvinylidene fluoride, polyacrylonitrile, cellulose acetate and regenerated cellulose as well as inorganic materials such as alumina, zirconia and titania. Most polymeric UF membranes are asymmetric in structure, i.e. they have a thin 'skin' 0.1–0.2 μm thick on the surface of the membrane. This skin contains the pores of the required size and determines the separation characteristics of the UF membrane. Polymer layers under the skin usually consist of voids which support the skin layer. The skin and void layer are one structure and one polymer when made by a phase-inversion process, but they could be two or more different polymers in composite membranes. The membrane is then laid on a backing such as polyester or polypropylene and then formed into the module. In some cases, such as hollow fibres, a concentrated solution of the polymer is spun or extruded to form self-supporting single polymer hollow tubes with the pores on the inside surface of the tube.

Inorganic membranes have considerably widened the range of membrane applications, particularly in food processing, waste treatment, recovery of chemicals and biotechnology applications, where high temperature, acid and/or alkali stability, steam sterilizability and cleanability are important. A macroporous substrate of a fine dispersion of the powder is first formed, e.g. by thermal sintering of an extruded paste of the powder. If a tubular geometry is used, pastes from two powders of different grain sizes may be co-extruded, with the finer grain being closer to the axis. After baking at high temperatures ($>1000^{\circ}C$), the inside may be coated by slip casting with the final fine grain powder. A series of such layers may be necessary to obtain the asymmetric-type ultrastructure. The membrane is finally set by a series of pressurizing, drying and baking steps. The most common ceramic materials are α-alumina, zirconia and titania. Composites of zirconia or titania membranes on alumina, carbon or stainless-steel supports are available.

Most inorganic membranes are available in tubular form, either as a single channel tube or multi-channel element, the latter containing up to 60 individual circular channels, depending on the relative diameters of the channel and the element. The inner diameter of individual channels vary from 2 to 6 mm and lengths from 0.8 to 1.2 m. As many as 99 of these elements may be put together in a single housing, resulting in

8–12 m^2 per module. Normal process ratings are 15 bar and 150°C.

Inorganic membranes have several desirable properties. They are inert to common chemicals and solvents and have wide temperature limits. Depending on the seals and type of housing, some inorganic membranes can be operated as high as 350°C and within wide limits of pH from 0.5 to 13.5. The biggest advantage is their extended operating lifetimes. Operating life of membranes is most affected by the frequency and nature of the cleaning regime. In contrast to polymeric membranes which typically have 9–18-month lifetimes with normal daily cleaning cycles, inorganic membranes are able to tolerate frequent aggressive cleaning regimes. Many are still operating 10–14 years after installation with the first set of membranes. One major limitation is that they are 10–30 times more expensive than polymeric membranes.

Membrane Properties

Pore size is the most important property of a UF membrane. Pores can be visualized using electron microscopy. Surface porosity (the proportion of the membrane surface occupied by pores) is less than 10% for many UF membranes. In an ideal membrane, all pores should be of the same size. In reality, there is a distribution of pore sizes, as shown in **Figure 3**. This makes it difficult to get a sharp separation of similarly sized molecules by UF. A common method to characterize UF membranes is to challenge the membrane with several macromolecules of known molecular sizes. Since proteins of different molecular weights are usually used as molecular markers, UF membranes are characterized in terms of their ability to retain proteins of a particular molecular weight. Figure 3 is a graphical representation of solute rejection data for ideal and real membranes. No membrane will display the sharp pore-size distribution shown for the ideal membrane. MF membranes are given 'absolute' ratings which is the largest particle that will be retained by the membrane, based on actual tests under standard conditions. In contrast, UF membranes are given 'nominal' ratings which refer to the molecular weight of a test solute (ideally it should be a globular protein) which is 90% rejected by the membrane under standard conditions. This rating is termed the molecular weight cut-off (MWCO) of the membrane.

Proteins are not ideal compounds to use for this purpose, since their molecular size can be affected by pH, ionic strength and interactions with buffer components. Proteins can have different isoelectric points, solubility and hydrophobicity, thus causing them to interact with and foul the membrane to different extents, which affects measured rejections. In addition, proteins which differ by 10 times in MW may only differ by three times in size in their globular form. Owing to the difficulty of finding proteins that are sufficiently pure (and inexpensive) to conduct MWCO evaluations, other compounds such as polyethylene glycols (PEG) and dextrans have been used because they are water soluble and can be readily obtained with well-defined and narrow-size distributions. Since the shapes of these various compounds are different, the MWCO profile of a membrane will also differ depending on the solute test marker used. Environmental conditions such as pH and ionic strength also affect shape and conformation of molecules which can affect rejection.

Other components in the feed solution could affect the separation of the target compound. For example, with UF membranes, low-molecular-weight solutes (such as sugars and salts) have molecular sizes much smaller than the smallest pore on the membrane. These compounds will be freely permeable, i.e. they will have zero rejection, unless they interact with or bind to impermeable compounds in the feed. Changes in operating conditions will not affect their permeability. On the other hand, large solutes that are much bigger than the pores will be completely rejected (i.e. 100% rejection). Its rejection properties will also be relatively unaffected by operating conditions or if other compounds are present. However, if the solute has a size that is of the same order of magnitude as the pore, its rejection may be affected in the presence of the large molecule. This is because the large molecule forms a secondary

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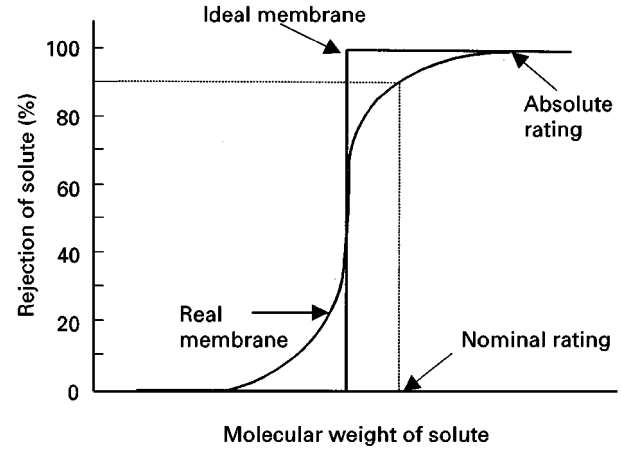

Figure 3 Typical molecular-weight profile of ideal and real membranes. Relationship shown is between molecular size of a solute in the feed stream and rejection of the solute by the membrane. (Adapted from Cheryan (1998) with permission from Technomic.)

dynamic membrane on the original membrane that inhibits passage of the smaller molecule. Operating conditions that change the shape or conformation of the solute will also affect its rejection.

As a general rule, fractionation of polymers can be accomplished if there is at least a 10-fold difference in molecular weight. Separation of similarly sized macromolecules can be enhanced by diluting the feed to minimize solute–solute interactions and solute-membrane interactions.

Other factors affecting separation are operating parameters such as pressure and cross-flow rate. These control the degree of turbulence and the thickness of the boundary layer and extent of concentration polarization (defined below), which in turn affect permeability of smaller solutes.

Operating Parameters

Separation of solutes by UF membranes occurs by a sieving mechanism. The transport of fluids through the pores is modelled as laminar flow through channels, with flux directly proportional to applied transmembrane pressure. However, it has frequently been observed that under certain operating conditions, flux becomes independent of pressure as shown in **Figure 4**. This is owing to 'concentration polarization' which is shown in **Figure 5**. Molecules or particles that are partially or completely retained by the membrane accumulate on the surface of the membrane during ultrafiltration. This build-up of solids will cause a concentration gradient within the boundary layer, resulting in back-transport of solute into the bulk stream owing to diffusion. Eventually a steady state is reached where the two phenomena balance each other. Solute concentration reaches a maximum at the 'gel concentration'. This consolidated gel layer is the reason that pressure independence in Figure 4 is observed. Flux is no longer controlled by pressure but by the mass-transfer characteristics of the system which in turn depends on the diffusion coefficient of the rejected molecules in the boundary layer, turbulence in the flow channel, viscosity and density of the fluid stream. Higher temperatures lead to higher flux because of its favorable effect on diffusivity and viscosity. In the pressure-independent region, flux decreases in a semi-logarithmic manner with bulk feed concentration and increases with higher turbulence (usually achieved by higher flow rates through the module).

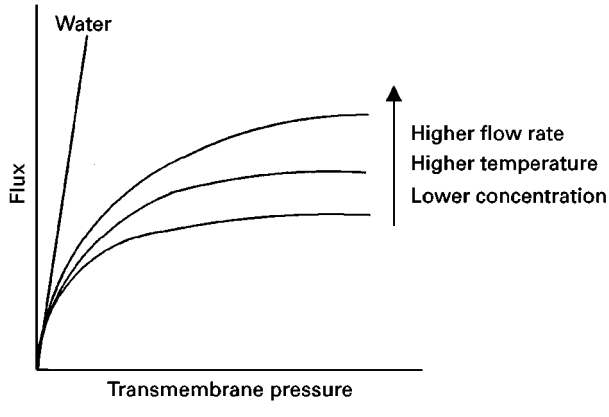

Figure 4 Effect of operating conditions on flux of an ultrafiltration system. (Adapted from Cheryan (1998) with permission from Technomic.)

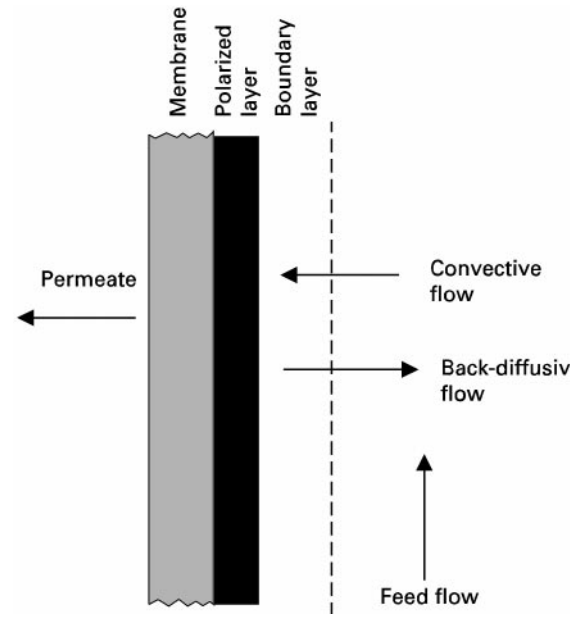

Figure 5 Concentration polarization in ultrafiltration.

Module Design

There are basically six different designs of membrane modules: tubular (with channel diameters greater than 3 mm), hollow fibre or capillaries (self-supporting tubes, usually 2 mm or less internal diameters), plates, spiral-wound, pleated sheets and moving modules (e.g. rotating discs or cylinders). **Figure 6** shows the more common types of modules. The selection of a particular design depends on (a) the physical properties of the feed stream and retentate, especially viscosity and osmotic pressure, (b) particle size of suspended matter in the feed, (c) fouling potential of the feed stream, and (d) sanitation requirements, such as cleanability and sterilizability. The viscosity of feed streams containing macromolecules such as polymers or proteins will increase nonlinearly with concentration above a certain value. This will require

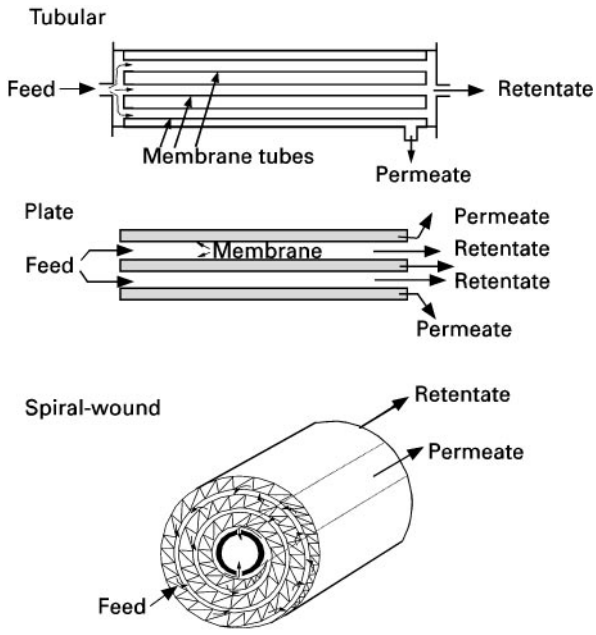

Figure 6 Schematic of ultrafiltration membrane modules: tubular, plate and spiral-wound.

high pressure drops for pumping and require the use of modules that can withstand high pressures, eliminating most hollow fibre/capillary modules. On the other hand, these modules have extremely high packing densities (surface area : volume ratios) and comparatively low energy consumption, making them useful in applications where the feed is of relatively low viscosity and low in suspended matter.

Spiral-wound modules and some plate modules incorporate a spacer in the feed channel to keep the membrane sandwich apart. This spacer can add considerable turbulence to the fluid flow and thus increase the flux. However, this spacer causes a parasitic drag and creates dead spots in the feed channel, which can cause suspended particles to block the flow channel, resulting in high pressure and cleaning problems.

Fouling and Cleaning

Fouling manifests itself as a decline in flux with time under constant operating conditions. The sieving properties of the membrane may also change. This is owing to irreversible interactions between feed components and the membrane, causing a layer of foulant on the membrane, blinding of the pores and an increased resistance to fluid flow through the membrane. Many membrane materials listed earlier are relatively hydrophobic (e.g. polysulfone, polyvinylidene fluoride) and tend to foul more than hydrophilic membrane materials (e.g. cellulosics, ceramics). Many feed components interact strongly with membranes, e.g. oils through hydrophobic interactions with hydrophobic membranes, proteins by hydrogen bonding, charge interactions or hydrophobic interactions, and salts by precipitation or charge interaction.

A fouled membrane has to be cleaned according to the nature of the foulant. Proteins can be effectively cleaned with alkaline solutions, salts are removed with acid cleaners. The quality of the water is very important in ensuring a membrane can be effectively cleaned in the shortest time possible.

Flux can be enhanced by periodic backwashing, pulsating flows, uniform transmembrane pressure or co-current permeate flow techniques. These have been found to be effective in maintaining high fluxes with feed streams containing colloidal or suspended matter and less effective with foulants that are in solution.

Applications of Ultrafiltration

Table 1 is a listing of ultrafiltration applications. The food industry has been one of the most successful users of UF, starting from the early 1970s when it was used to treat cheese whey to recover the protein. Another successful application has been electrocoat painting, where the UF system is used to maintain the ionic balance of the painting system and to recover paint that has been washed off. Biotechnology has benefited tremendously by UF, where it finds its greatest use in the production of pyrogen-free water and for fractionation, purification and concentration

Table 1 Applications of ultrafiltration

Food industry
Concentration of protein and fat for cheese manufacture; fractionation of cheese whey for whey protein concentrates; clarification of fruit juices (apple, apricot, citrus, cranberry, grape, peach, pear, pineapple; gelatin concentration and de-ashing; eggs concentration and reduction of glucose; animal blood concentration; soybean protein concentrates and isolates; clarification of protein hydrolysates; vegetable oils (degumming, deacidification, bleaching, removal of metals, dewaxing; clarifying frying oils); sugar refining; dextrose clarification; alcoholic beverages
Chemicals and wastewater
Electrocoat paint; oily wastewater; stillage from bioethanol plants; caustic and acid recovery; brine recovery; printing ink; laundry wastewater; textile industry; latex emulsions; pulp and paper industry; tanning and leather industries; fish processing; poultry industry
Biotechnology
Separation and harvesting of microbial cells; enzyme recovery; affinity ultrafiltration; membrane bioreactors

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of proteins and other macromolecules. Continued advances in membrane science and manufacture and engineering improvements to modules and systems will allow a greater penetration of this technology in a variety of industries in the future.

See also: **II/Membrane Separations:** Filtration; Microfiltration.

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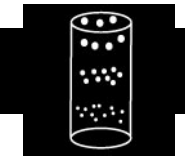
PARTICLE SIZE SEPARATION: Electric Fields in Field Flow Fractionation

See **II / PARTICLE SIZE SEPARATION / Field Flow Fractionation: Electric Fields**

PARTICLE SIZE SEPARATION



Electrostatic Precipitation

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Introduction

Electrostatic precipitators (ESPs) are the most commonly used devices for the removal of fine particles in exhaust from industrial and utility processes. Wire-plate ESPs consist of three or more sections of arrays of large (e.g., 15 m × 5 m), grounded metal collector plates between which are situated wire or other narrow, high voltage electrodes (**Figure 1**). Less commonly, a wire-cylinder electrode configuration is used. Particles entering the first section are quickly charged by ions generated by the plasma coronas around the wires. (Current does pass between the electrodes, hence the term 'electrostatic' is not really accurate, but indicates the small current-to-electrode area.) The charged particles are drawn toward and deposit upon the collector plates, which are periodically cleaned by mechanical 'rapping'. This method is very efficient in removing particles in the 1– >10 μm range. The most common use of ESPs is in control of exhaust from coal combustion utilities. Precipitators are also used in the cement, ore smelting, steel production, pulp and paper manufacturing, and chemical processing industries, and in waste combustion utilities. Small units are used in cleaning domestic and workplace air, and have been considered for use in animal production facilities.

M. Holfield first demonstrated the removal of particles by electrostatic charging in 1820. Holfield showed that tobacco smoke can be cleared in a bottle by applying a spark-producing voltage to a pointed electrode inserted in the bottle. In 1850, C. F. Guitard observed that a steady corona discharge is effective in dissipating smoke. Sir Oliver Lodge first attempted